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**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

GRI-01-013

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5)

09/914638

INTERNATIONAL APPLICATION NO.

PCT/US00/05735

INTERNATIONAL FILING DATE

03 March 2000

PRIORITY DATE CLAIMED

03 March 1999

TITLE OF INVENTION

METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

APPLICANT(S) FOR DO/EO/US

Raymond J. GORTE et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND OR SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (unexecuted, attached to a copy of the International Application)
 10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☐ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
 14. ☐ A substitute specification.
 15. ☐ A change of power of attorney and/or address letter.
 16. ☒ Other items or information:
 - Form PCT/IB/301
 - Form PCT/IB/304
 - Form PCT/IB/308
 - Form PCT/ISA/210 (4 pages)
 - Certificate of Mailing by Express Mail (2 pages)
 - Return Receipt Postcard

EXPRESS MAIL NO.: EL815472768US

MAILED: 31 August 2001

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/914638

INTERNATIONAL APPLICATION NO

PCT/US00/05735

ATTORNEY'S DOCKET NUMBER

GRI-01-013

17. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO \$ 860.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) \$ 690.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482)
but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$ 710.00Neither international preliminary examination fee (37 CFR 1.482) nor
international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$ 1,000.00International preliminary examination fee paid to USPTO (37 CFR 1.482) and
all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00**CALCULATIONS**

PTO USE ONLY

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$ 860.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from
the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS

NUMBER FILED

NUMBER EXTRA

RATE

Total claims

20* - 20 =

0

X \$18.00

\$ 0.00

Independent claims

4* - 03 =

1

X \$80.00

\$ 80.00

MULTIPLE DEPENDENT CLAIM(S) (if applicable)

+ \$270.00

TOTAL OF ABOVE CALCULATIONS =

\$ 940.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement
must also be filed (Note 37 CFR 1.9, 1.27, 1.28).**SUBTOTAL =**

\$ 940.00

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months
from the earliest claimed priority date (37 CFR 1.492(f)).

+

TOTAL NATIONAL FEE =

\$ 940.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an
appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property

+

TOTAL FEES ENCLOSED =

\$ 940.00

Amount to be:
refunded

\$

charged

\$

* Based upon Article 19 Amendment.

a. ☒ A check in the amount of \$ 940.00 to cover the above fee is enclosed.b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 19-3550. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b))
must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Pauley Petersen Kinne & Fejer
2800 West Higgins Road, Suite 365
Hoffman Estates, Illinois 60195
(847) 490-1400
Fax: (847) 490-1403

SIGNATURE

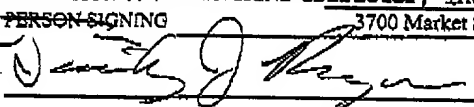
Mark E. Fejer

NAME

34,817

REGISTRATION NUMBER

PTO/SB/11 (10-92)

VERIFIED STATEMENT CLAIMING SMALL ENTITY STATUS (37 CFR 1.9(f) & 1.27(d))--NONPROFIT ORGANIZATION		Docket Number GRI-01-013
Applicant or Patentee:	<u>Raymond J. GORTE et al.</u>	
Serial or Patent No.:	<u>09/914,638</u>	
Filed or Issued:		
Title:	<u>METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION</u>	
I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:		
NAME OF NONPROFIT ORGANIZATION	<u>University of Pennsylvania</u>	
ADDRESS OF NONPROFIT ORGANIZATION	<u>3700 Market Street, Suite 300</u> <u>Philadelphia, Pennsylvania 19104-3147</u>	
TYPE OF NONPROFIT ORGANIZATION:		
<input checked="" type="checkbox"/> UNIVERSITY OR OTHER INSTITUTION OF HIGHER EDUCATION		
<input type="checkbox"/> TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 U.S.C. 501(a) and 501(c)(3))		
<input type="checkbox"/> NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA		
NAME OF STATE	<u></u>	
CITATION OF STATUTE	<u></u>	
<input type="checkbox"/> WOULD QUALIFY AS TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 U.S.C. 501(a) and 501(c)(3)) IF LOCATED IN THE UNITED STATES OF AMERICA		
<input type="checkbox"/> WOULD QUALIFY AS NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA IF LOCATED IN THE UNITED STATES OF AMERICA		
NAME OF STATE	<u></u>	
CITATION OF STATUTE	<u></u>	
I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 CFR 1.9(e) for purposes of paying reduced fees to the United States Patent and Trademark Office regarding the invention described in:		
<input type="checkbox"/> the specification filed herewith with title as listed above.		
<input checked="" type="checkbox"/> the application identified above		
<input type="checkbox"/> the patent identified above.		
I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization regarding the above identified invention. If the rights held by the nonprofit organization are not exclusive, each individual, concern or organization having rights in the invention must file separate verified statements averring to their status as small entities and that no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).		
Each person, concern or organization having any rights in the invention is listed below:		
<input type="checkbox"/> no such person, concern or organization exists.		
<input checked="" type="checkbox"/> each such person, concern or organization is listed below:		
Gas Research Institute 1700 South Mount Prospect Road Des Plaines, Illinois 60018-1804		
I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b)).		
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.		
NAME OF PERSON SIGNING <u>Timothy J. Raynor</u>		
TITLE IN ORGANIZATION OF PERSON SIGNING <u>Director, Intellectual Property</u>		
ADDRESS OF PERSON SIGNING <u>3700 Market Street, Suite 300, Philadelphia, Pennsylvania 19104-3147</u>		
SIGNATURE		DATE <u>11/29/01</u>

RECEIVED

**VERIFIED STATEMENT CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) & 1.27(d))--NONPROFIT ORGANIZATION**
Docket Number
GRI-01-013

Applicant or Patentee: Raymond J. GORTE et al.
 Serial or Patent No.: 09/914,638
 Filed or Issued: _____
 Title: METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF NONPROFIT ORGANIZATION Gas Research Institute
 ADDRESS OF NONPROFIT ORGANIZATION 1700 South Mount Prospect Road
Des Plaines, Illinois 60018-1804

TYPE OF NONPROFIT ORGANIZATION:

- ☐ UNIVERSITY OR OTHER INSTITUTION OF HIGHER EDUCATION
- ☒ TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 U.S.C. 501(a) and 501(c)(3))
- ☐ NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA
 NAME OF STATE _____
 CITATION OF STATUTE _____
- ☐ WOULD QUALIFY AS TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 U.S.C. 501(a) and 501(c)(3)) IF LOCATED IN THE UNITED STATES OF AMERICA
- ☐ WOULD QUALIFY AS NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA IF LOCATED IN THE UNITED STATES OF AMERICA
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 CITATION OF STATUTE _____

I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 CFR 1.9(e) for purposes of paying reduced fees to the United States Patent and Trademark Office regarding the invention described in:

- ☐ the specification filed herewith with title as listed above.
☒ the application identified above.
☐ the patent identified above.

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization regarding the above identified invention. If the rights held by the nonprofit organization are not exclusive, each individual, concern or organization having rights in the invention must file separate verified statements averring to their status as small entities and that no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern or organization having any rights in the invention is listed below:

- ☐ no such person, concern or organization exists.
☒ each such person, concern or organization is listed below:

University of Pennsylvania
 3700 Market Street, Suite 300
 Philadelphia, Pennsylvania 19104-3147

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b)).

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Thomas C. O'Laughlin
 TITLE IN ORGANIZATION OF PERSON SIGNING General Counsel and Secretary
 ADDRESS OF PERSON SIGNING 1700 South Mount Prospect Road, Des Plaines, Illinois 60018-1804

SIGNATURE Thomas C. O'Laughlin DATE Oct. 9, 2001

**VERIFIED STATEMENT CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) & 1.27(d))--NONPROFIT ORGANIZATION**
**Docket Number
GRI-01-013**

Applicant or Patentee: Raymond J. GORTE et al.
 Serial or Patent No.: 09/914,638
 Filed or Issued: _____
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I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF NONPROFIT ORGANIZATION University of Pennsylvania
 ADDRESS OF NONPROFIT ORGANIZATION 3700 Market Street, Suite 300
Philadelphia, Pennsylvania 19104-3147

TYPE OF NONPROFIT ORGANIZATION:

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 NAME OF STATE _____
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- ☐ WOULD QUALIFY AS NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA IF LOCATED IN THE UNITED STATES OF AMERICA
 NAME OF STATE _____
 CITATION OF STATUTE _____

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- ☐ the specification filed herewith with title as listed above.
☒ the application identified above.
☐ the patent identified above.

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Each person, concern or organization having any rights in the invention is listed below:

- ☐ no such person, concern or organization exists.
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Gas Research Institute
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Timothy J. Raynor
 TITLE IN ORGANIZATION OF PERSON SIGNING Director, Intellectual Property
 ADDRESS OF PERSON SIGNING 3700 Market Street, Suite 300, Philadelphia, Pennsylvania 19104-3147

SIGNATURE  DATE 11/29/01

METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

BACKGROUND OF THE INVENTION

Field of the Invention

5 This invention relates to a method for preparation of anodes for use in solid oxide fuel cells. More particularly, this invention relates to a method for preparation of an anode for a solid oxide fuel cell in which metals and catalytic materials employed in such anodes are added in a separate step compared to conventional methods of anode preparation.

Description of Prior Art

10 Solid oxide fuel cells have grown in recognition as a viable high temperature fuel cell technology. There is no liquid electrolyte with its attending metal corrosion and electrolyte management problems. Rather, the electrolyte of the cells is made primarily from solid ceramic materials so as to survive the high temperature environment. The operating temperature of greater than about 600°C allows internal reforming, promotes rapid kinetics with non-precious materials, and produces high quality by-product heat for cogeneration or
15 for use in a bottoming cycle. The high temperature of the solid oxide fuel cell, however, places stringent requirements on its materials. Because of the high operating temperatures of conventional solid oxide fuel cells (approximately 1000°C), the materials used in the cell components are limited by chemical stability in oxidizing and reducing environments, chemical stability of contacting materials, conductivity, and thermomechanical compatibility.
20

The most common anode materials for solid oxide fuel cells are nickel (Ni)-cermets prepared by high-temperature calcination of NiO and yttria-stabilized zirconia (YSZ) powders. High-temperature calcination is essential in order to obtain the necessary ionic conductivity in the YSZ. These Ni-cermets perform well for hydrogen (H₂) fuels and
25 allow internal steam reforming of hydrocarbons if there is sufficient water in the feed to the anode. Because Ni catalyzes the formation of graphite fibers in dry methane, it is necessary to operate anodes at steam/methane ratios greater than 3. However, there are significant advantages to be gained by operating under dry conditions. Progress in this area has been made using an entirely different type of anode, either based on ceria (See Eguchi, K, et al.,
30 Solid State Ionics, 52, 165 (1992); Mogensen, G., Journal of the Electrochemical Society,

141, 2122 (1994); and Putna, E.S., et al., Langmuir, 11 4832 (1995)) or perovskite anodes (See Baker, R.T., et al., Solid State Ionics, 72, 328 (1994); Asano, K., et al., Journal of the Electrochemical Society, 142, 3241 (1995); and Hiei, Y., et al., Solid State Ionics, 86-88, 1267 (1996)). These oxides do not, however, provide sufficient electronic conductivity.

5 Replacement of Ni for other metals, including Co (See Sammes, N.M., et al., Journal of Materials Science, 31, 6060 (1996)), Fe (See Bartholomew, C.H., Catalysis Review-Scientific Engineering, 24, 67 (1982)), Ag or Mn (See Kawada, T., et al., Solid State Ionics, 53-56, 418 (1992)) has been considered; however, with the possible exception of Ag, these are likely to react with hydrocarbons in a way similar to that of Ni. Substitution of Ni with

10 Cu would also be promising but for the fact that CuO melts at the calcination temperatures which are necessary for establishing the YSZ matrix in the anodes.

It is also well known that the addition of ceria to the anode improves performance. However, the high-temperature calcination utilized in conventional anode preparation causes ceria to react with YSZ, as a result of which performance is not enhanced to the extent which could be possible if formation of ceria-zirconia did not occur.

15

SUMMARY OF THE INVENTION

Accordingly, it is one object of this invention to provide a method for preparation of solid oxide fuel cell anodes which enables the use of lower melting temperature materials than employed by conventional solid oxide fuel cell anodes.

20 It is another object of this invention to provide a process for solid oxide fuel cell anode preparation which enables efficient operation using dry natural gas as a fuel.

It is another object of this invention to provide a method for generation of electricity by direct oxidation of hydrocarbons and other carbonaceous fuels.

25 It is yet another object of this invention to provide a method for a solid oxide fuel cell anode preparation which enables the use of ceria to improve anode performance while avoiding the formation of ceria-zirconia which reduces the extent of performance enhancement in conventional solid oxide fuel cell anodes.

30 These and other objects of this invention are addressed by a method for preparation of an anode for a solid oxide fuel cell in which a plurality of zircon fibers or other porous matrix material is mixed with a yttria-stabilized-zirconia (YSZ) powder, thereby

forming a fiber/powder mixture. The fiber/powder mixture is then formed into a porous YSZ layer and calcined. The calcined porous YSZ layer is then impregnated with a metal-containing salt solution. Accordingly, contrary to conventional methods for solid oxide fuel cell anode preparation, the method of this invention results in a YSZ layer which remains highly porous following high-temperature calcination to which any suitable metal, including Cu and Ni is then added by impregnation of the salt solution, after the high temperature calcination of the YSZ layer. In addition to enabling the use of metals whose oxides have a low melting temperature, the method of this invention also allows catalytic materials, such as ceria and/or palladium (Pd) to be added in controlled amounts in a separate step.

Cells prepared in accordance with the method of this invention with Ni perform in a very similar manner to those cells prepared using conventional means. With Cu used in place of Ni, there is a possibility of oxidizing hydrocarbons (C_xH_y) and other carbonaceous fuels ($C_xH_yO_z$) such as methanol, ethanol, propanol and the like directly, particularly since Cu is inert in dry methane. Even without direct conversion, the Cu-YSZ anode allows the use of dryer gases (partially reformed methane), because Cu is inert to methane. To convert methane, it is necessary to add a catalytic component. Ceria, particularly when doped with noble metals like Pd, Pt, or Rh, is active for this process.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and features of this invention will be better understood from the following detailed description taken in conjunction with the drawings wherein:

Fig. 1 is a diagram showing the I-V relationship for cells at 800°C in H_2 prepared by impregnating porous YSZ with 40% Cu in accordance with one embodiment of this invention;

Figs. 2A, 2B, and 2C show SEM micrographs for conventional Ni-cermet prepared from NiO and dense yttria-stabilized zirconia, designated as YSZd, neat porous yttria-stabilized zirconia designated as YSZp, and Cu-cermet prepared from 25% YSZd impregnated with 40% Cu, respectively;

Fig. 3 is a diagram showing the I-V relationship for cells at 800°C in H_2 prepared by impregnating porous YSZ (25% YSZd) with varying amounts of Cu;

Fig. 4 is a diagram showing the I-V relationship for cells at 800°C in H₂ with a conventional Ni-cermet anode, a Ni-cermet anode prepared from porous YSZ (25% YSZd), and Cu-cermet prepared from porous YSZ (25% YSZd);

Fig. 5 is a diagram showing the I-V relationship for cells at 800°C in H₂ with the addition of ceria to Cu/YSZp;

Fig. 6 is a diagram showing the I-V relationship for cells at 800°C in H₂ with the addition of ceria to Cu/YSZ mixture;

Fig. 7 is a diagram showing current density as a function of time for Ni- and Cu-based cells during switching of fuels from dry H₂ to dry CH₄ and back; and

Fig. 8 is a diagram showing the I-V relationship for Cu-based cells with methane.

DESCRIPTION OF PREFERRED EMBODIMENTS

As previously stated, conventional solid oxide fuel cells are unable to operate efficiently in dry natural gas. This is due to the fact that they typically have Ni-cermet anodes which are prepared by high-temperature calcination of powders consisting of NiO and yttria-stabilized zirconia. High-temperature calcination is essential in order to obtain the necessary ionic conductivity in the YSZ. Under the reducing conditions of operation, NiO is reduced to the metal and provides electronic conductivity. However, in dry methane, Ni tends to form graphite fibers which quickly deactivate the system. Ni can be replaced by Fe or Co, but these metals suffer from similar problems. We have developed a method for preparation of an anode for a solid oxide fuel cell which allows the addition of the electron-conducting metal, including metals like Cu, for which the oxide melts at low temperature, in a manner which does not require the high-temperature calcination of conventional methods. In addition, catalytic and ion-transfer components, such as ceria, lanthana, manganese, and precious metals can also be added without further, high-temperature treatment.

In accordance with the method of this invention, a plurality of zircon fibers or other porous matrix material is mixed with a yttria-stabilized-zirconia powder, forming a fiber/powder mixture. The fiber/powder mixture is formed into a porous YSZ layer and calcined. After calcination, the porous YSZ layer is impregnated with a metal-containing salt

solution. In accordance with one preferred embodiment of this invention, the metal-containing salt solution comprises a nitrate salt of a metal selected from the group consisting of Cu, Ni and mixtures thereof.

In accordance with one preferred embodiment of this invention, the fiber/powder mixture is made into a slurry with glycerol and then applied to the anode side of the dense YSZ electrolyte of a solid oxide fuel cell. In accordance with another preferred embodiment, the powdered fibers are added to a tapecast which can be included as a layer in a composite with a second layer which will give dense YSZ. The system is then calcined at a suitable temperature, for example 1550°C, for two hours. After addition of the cathode to the cathode side of the YSZ electrolyte, the porous YSZ layer on the anode side is impregnated with aqueous solutions of $\text{Ni}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ to bring the metal content of the anode to at least 35% by weight metal, after which the anode is calcined at 950°C for two hours. It is very important either to mix a normal YSZ powder (about 20% by weight) with the zircon fibers in the original glycerol slurry, or to add ceria or YSZ to the porous YSZ layer so as to provide sufficient oxide in the anode for ionic conductivity. Ceria in accordance with one embodiment of this invention is added using an aqueous solution of $\text{Ce}(\text{NO}_3)_3$ to the porous anode, after addition of the metal. After drying, the anode is again calcined to 900°C to form the oxide or ceria. In accordance with a particularly preferred embodiment of this invention, ceria constitutes in the range of about 5% to about 40% by weight of the porous YSZ layer.

Example

Yttria-stabilized zirconia (8% Y_2O_3 , Tosoh TZ-8Y, denoted as YSZd) was used for the fabrication of the electrolyte and conventionally prepared anode for a solid oxide fuel cell. The electrolyte wafers were formed from YSZd by tapecasting, followed by calcination to 1400°C for two hours. The cathodes were formed from a 50% by weight physical mixture of Sr-LaMnO_3 and YSZd powders, pasted onto the electrolyte with glycerol, and then calcined at 1250°C for two hours. The conventional, Ni-cermet anode was prepared using a 50% by weight physical mixture of NiO and YSZd, followed by calcination to 900°C. This Ni-cermet was pasted onto the electrolyte using glycerol and calcined to 1400°C.

In accordance with the method of this invention for preparation of an anode for a solid oxide fuel cell, a porous YSZ layer was prepared from physical mixtures of zircon fibers (YSZ, 75% porosity, with less than about 0.3% Si, Zircar Products, Inc., denoted as YSZp) and YSZd. The physical mixture (denoted as YSZm) was pasted onto the electrolyte using glycerol and calcined to 1550°C for two hours. After addition of the cathode, the porous YSZ layer was impregnated with aqueous solutions of $\text{Cu}(\text{NO}_3)_2$ (Fisher Scientific) or $\text{Ni}(\text{NO}_3)_2$ (Aldrich) followed by calcination at 950°C for two hours, at a Cu (or Ni) content of 40% by weight.

A sample doped with ceria was prepared by adding ceria in an amount of about 5 to about 40 weight percent of the anode material, to the anode by impregnation using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) followed by calcination to 950°C. The fraction of YSZd used in the anode and the metal content of the anode were varied.

Pt electrodes were attached to both anodes and cathodes using a Pt ink (Engelhard, A4338), followed by calcination at 950°C for thirty minutes. The cells were sealed into Al_2O_3 tubes using quartz powder in polyvinyl solutions. They were then conditioned in H_2 for three to four hours at 950°C. The performance of the cells was measured using flowing H_2 at 1 atmosphere at the anode, and the cathode was open to air.

SEM images were obtained using a JEOL 6300 microscope equipped with an X-ray analyzer for EDX analysis. Samples were deposited onto carbon tape and coated with a gold film before analysis. X-ray powder diffraction patterns were obtained with a Rigaku XRD diffractometer, using Cu $K\alpha$ radiation ($\lambda = 1.541838 \text{ \AA}$). The mean crystallite size (\bar{d}) of YSZ particles was determined from XRD line-broadening measurements using the Scherrer equation.

Fig. 1 shows the performance for series of cells prepared with Cu-cermet anodes at 800°C. In this series, the Cu content was maintained at approximately 40% by weight, but the fraction of non-porous YSZd was varied. Performance for the pure zircon fibers (neat YSZp) was poor, giving a maximum power density of only 5.1 mW/cm² and a maximum current density of 35 mA/cm². Adding YSZd to the layer improved the performance significantly, with the best performance being achieved at about 25% by weight YSZd. The maximum power density for this cell was nearly 50 mW/cm², with a maximum

current density of 210 mA/cm². Increasing the fraction of YSZd in the layer led to poorer performance. The results in Fig. 1 demonstrate the importance of maintaining the proper structure of the YSZ in the anode as well as the possibility of a deleterious effect of Si in the zircon fibers.

5 Figs. 2A, 2B, and 2C show SEM pictures of several representative samples of anodes taken for the purpose of investigating their morphologies. Fig. 2A is a micrograph of the conventional Ni-cermet taken at a magnification of 5000x. Shown is a dense film made up of about 1-micron particles. Before exposure to H₂ (the fuel atmosphere), EDX analysis and XRD patterns show the presence of NiO particles as a physical mixture with the YSZ ($\bar{d} = 28.5$ nm). After exposure to H₂ at 950°-800°C (reducing atmosphere), NiO is reduced to Ni metal ($\bar{d} = 26$ nm), determining a small porosity (about 20%) to the compact NiO-YSZ material. The micrographs of the neat zircon fibers, shown in Fig. 2B at 1500x after heating to 1550°C, show rods, roughly 20 microns long and 5 microns in diameter. The film remains highly porous, about 70% void, but contact between the rods appears to be poorer. Finally, the film formed by adding 25% by weight YSZd and Cu in accordance with the method of this invention is shown in Fig. 2C. The structure remains open due to the rod-like fibers. Even with the addition of non-porous YSZd and significant amounts of Cu, the film remains highly porous. Before H₂ exposure, small crystallites of CuO ($\bar{d} = 12.3$ nm) were formed on the YSZm material. After H₂ exposure at 950°C, Cu metal particles ($\bar{d} = 34$ nm) are formed, as was observed in the Ni-cermet case.

The effect of changing the Cu content in the anode for the YSZm made from 25% by weight YSZd is shown in Fig. 3. As can be seen, there is a definite improvement in cell performance observed with increases in Cu from about 20% to about 50% by weight Cu.

Fig. 4 shows a comparison of results for a Ni-cermet anode prepared by conventional methods, a Ni-cermet with 40% Ni prepared from YSZm in accordance with one embodiment of this invention and a Cu-cermet with 40% by weight Cu prepared from YSZm in accordance with one embodiment of this invention. The results for all three cells are virtually identical, with maximum power densities between 45 and 50 mW/cm². The similarity in performance suggests that the performance of these three cells is limited by the electrolyte and cathodes and not the anodes. In addition, because the catalytic properties of

Ni and Cu are very different, with H_2 dissociation occurring much more readily on Ni, this suggests that the catalytic properties of the metals are not crucial in this application with H_2 fuels. Rather Ni and Cu are primarily electronic conductors in this case.

Figs. 5 and 6 show the typical doping effect of ceria on Cu/YSZp and Cu/YSZm prepared using the method of this invention. The data for these cells shows that the power densities increased significantly with the addition of ceria. For 40% by weight ceria addition to Cu/YSZp and Cu/YSZm, the best results achieved were 151.2 mW/cm² and 146.4 mW/cm², which compared to 5.1 mW/cm² and 46.6 mW/cm² obtained in the same cells without ceria. The measured current density on CeO₂/Cu/YSZp was much higher than neat Cu/YSZp according to ceria contents. However, the current density does not increase over 20% by weight ceria on Cu/YSZm. In such ceria content range, there is a limit to the improvement of cell performance obtained.

The effect of adding ceria and Pd, using dry methane as a fuel is shown in Figs. 7 and 8. Before discussing the I-V curves, it is important to address the stability issues. As expected, the Ni-YSZ anode prepared in accordance with the method of this invention deactivated rapidly. While we did observe currents at 800°C, they decreased rapidly over the period of a few minutes with the formation of a carbonaceous residue. This is shown in Fig. 7, which shows the current density for a Ni/CeO₂/YSZ (open circles) at a cell voltage of 0.5 volts with switching of fuels from dry H_2 to dry CH_4 and back. The cell with a Ni/CeO₂/YSZ anode deactivated rapidly. Visual inspection showed the presence of carbon. By contrast, the Cu/CeO₂/YSZ cells were entirely stable. Following exposure to dry CH_4 for up to three days, we observed no evidence of decreased performance or carbon formation.

The performance of the Cu-based cells with methane is shown in Fig. 8. For the Cu-YSZ anode, the OCV was only about 0.5 volts and the power density was minimal. Addition of ceria led to a dramatic improvement, as did the addition of Pd. However, the maximum power density with methane is still much lower than with hydrogen, about 80 mW/cm² compared to 165 mW/cm². This difference between methane and hydrogen is lowered by working at higher temperatures. At 900°C, the maximum power density achieved with this cell was about 230 mW/cm² with H_2 and 160 mW/cm² with CH_4 . This suggests that

the catalytic reaction is at least partly limiting the reaction with methane, but that reasonable performance can be achieved with dry methane if a catalytic component is added.

As demonstrated hereinabove, we have developed an entirely new method for fabricating anodes which allows the addition of metals and/or catalytic materials after the high-temperature calcination step. We have demonstrated that we can achieve similar performance levels with Cu-cermets as can be achieved with Ni-cermets. And, we have found that ceria plays an important role in anode design.

While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

WE CLAIM:

1. A method for preparation of an anode for a solid oxide fuel cell comprising the steps of:
 - mixing a porous matrix material with a yttria-stabilized-zirconia (YSZ) powder, forming a porous matrix material/powder mixture;
 - forming said porous matrix material/powder mixture into a porous YSZ layer;
 - calcining said porous YSZ layer; and
 - impregnating said porous YSZ layer with a Cu-containing salt solution.
2. A method in accordance with Claim 1, wherein said porous matrix material comprises a plurality of zircon fibers.
4. A method in accordance with Claim 1, wherein said porous matrix material/powder mixture is mixed with glycerol and applied to an anode side of a YSZ electrolyte, forming said porous YSZ layer on said anode side of YSZ electrolyte.
5. A method in accordance with Claim 1, wherein said porous matrix material/powder mixture is added to a tapecast and said tapecast is deposited onto an anode side of a YSZ electrolyte layer, forming said porous YSZ layer on said anode side of YSZ electrolyte.
6. A method in accordance with Claim 5, wherein a cathode is applied to a cathode side of said YSZ electrolyte layer after said calcining of said porous YSZ layer.
7. A method in accordance with Claim 1, wherein a metal content of said porous YSZ layer is at least about 35% by weight of said porous YSZ layer.
8. A method in accordance with Claim 1, wherein said impregnated porous YSZ layer is calcined.

9. A method in accordance with Claim 1, wherein said porous YSZ layer is impregnated with ceria.

10. A method in accordance with Claim 9, wherein said ceria constitutes in a range of about 5% to about 40% by weight of said porous YSZ layer.

11. A method for producing a solid oxide fuel cell comprising the steps of:

mixing a porous matrix material with a yttria-stabilized-zirconia (YSZ) powder, forming a porous matrix material/powder mixture;

mixing said porous matrix material/powder mixture with glycerol, forming a slurry;

applying said slurry to an anode-facing face of a dense YSZ electrolyte layer, forming a porous anode layer/electrolyte layer assembly;

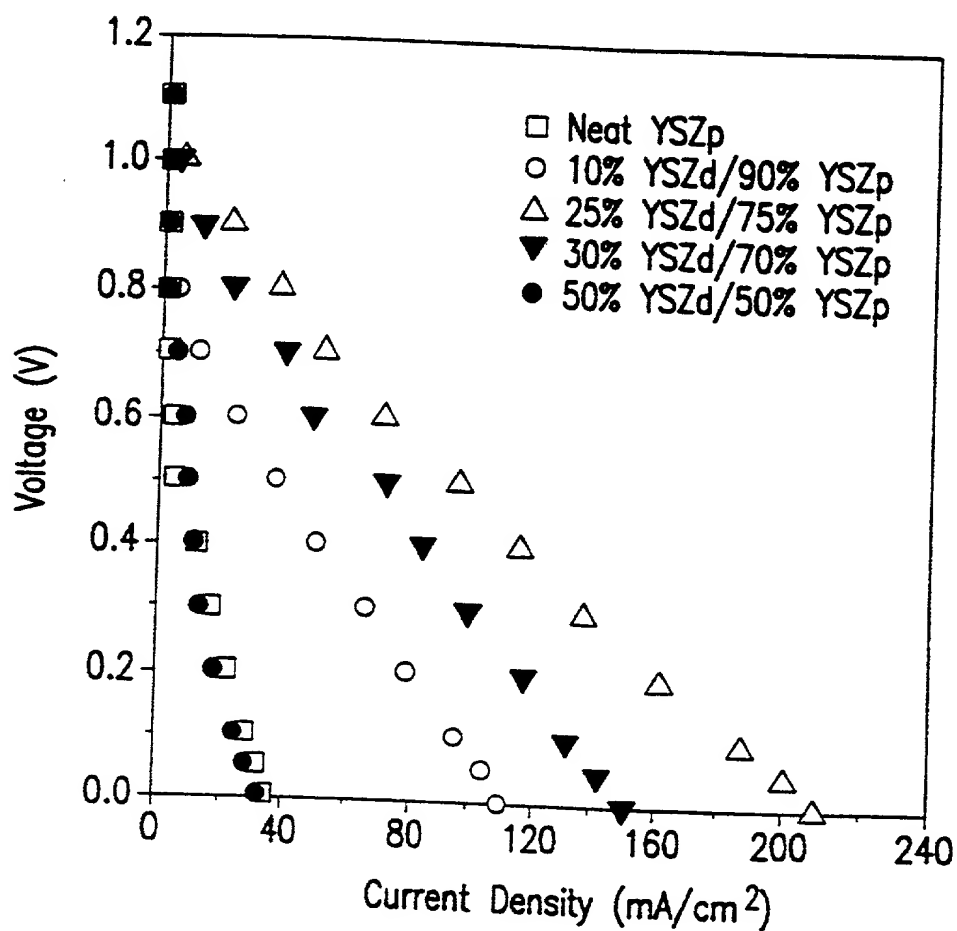
calcining said porous anode layer/electrolyte layer assembly;

applying a cathode layer to a cathode-facing face of said electrolyte layer, forming a fuel cell assembly;

impregnating said porous anode layer with a Cu-containing salt solution; and calcining said impregnated porous anode layer.

13. A method in accordance with Claim 12, wherein a metal content of said calcined impregnated porous anode layer is at least about 35% by weight of said calcined impregnated porous anode layer.

14. A method in accordance with Claim 11, wherein said porous matrix material comprises a plurality of zircon fibers.



YSZd = dense YSZ

YSZp = porous YSZ

□, $P_{max} = 5.1 \text{ mW/cm}^2$ ○, $P_{max} = 19.4 \text{ mW/cm}^2$ △, $P_{max} = 34.6 \text{ mW/cm}^2$ ▼, $P_{max} = 4.0 \text{ mW/cm}^2$ ●, $P_{max} = 46.6 \text{ mW/cm}^2$

FIG.1

FIG. 2A

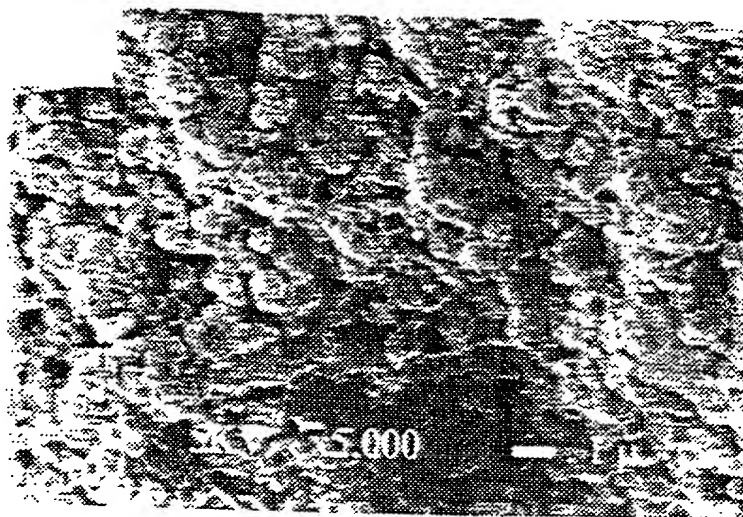


FIG. 2B

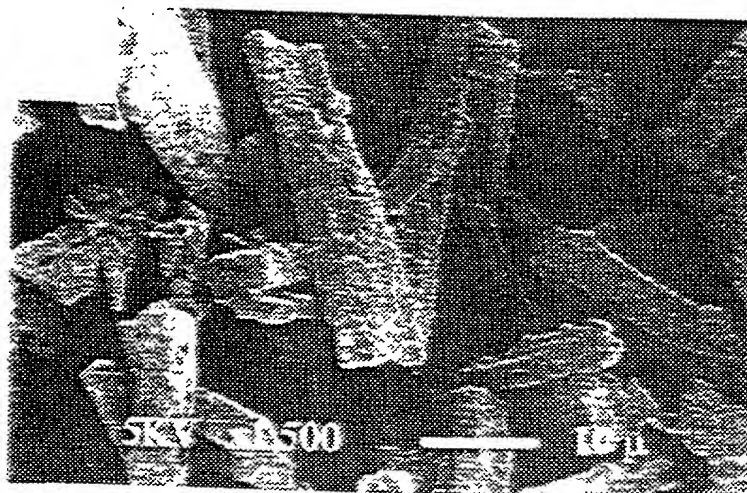
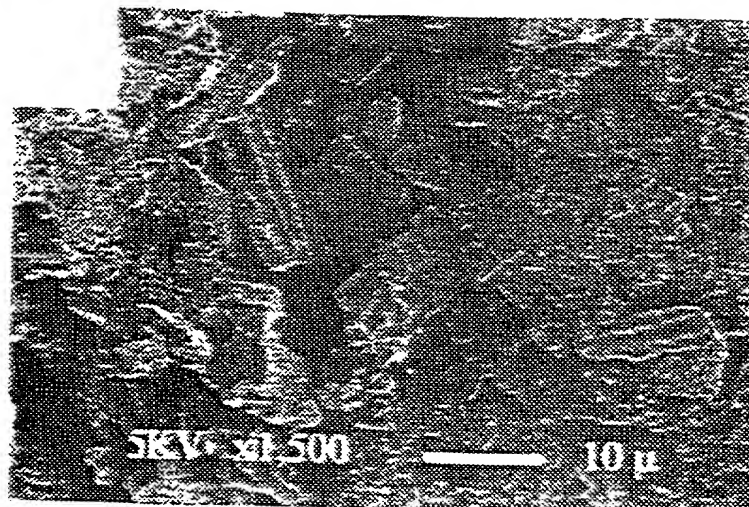


FIG. 2C



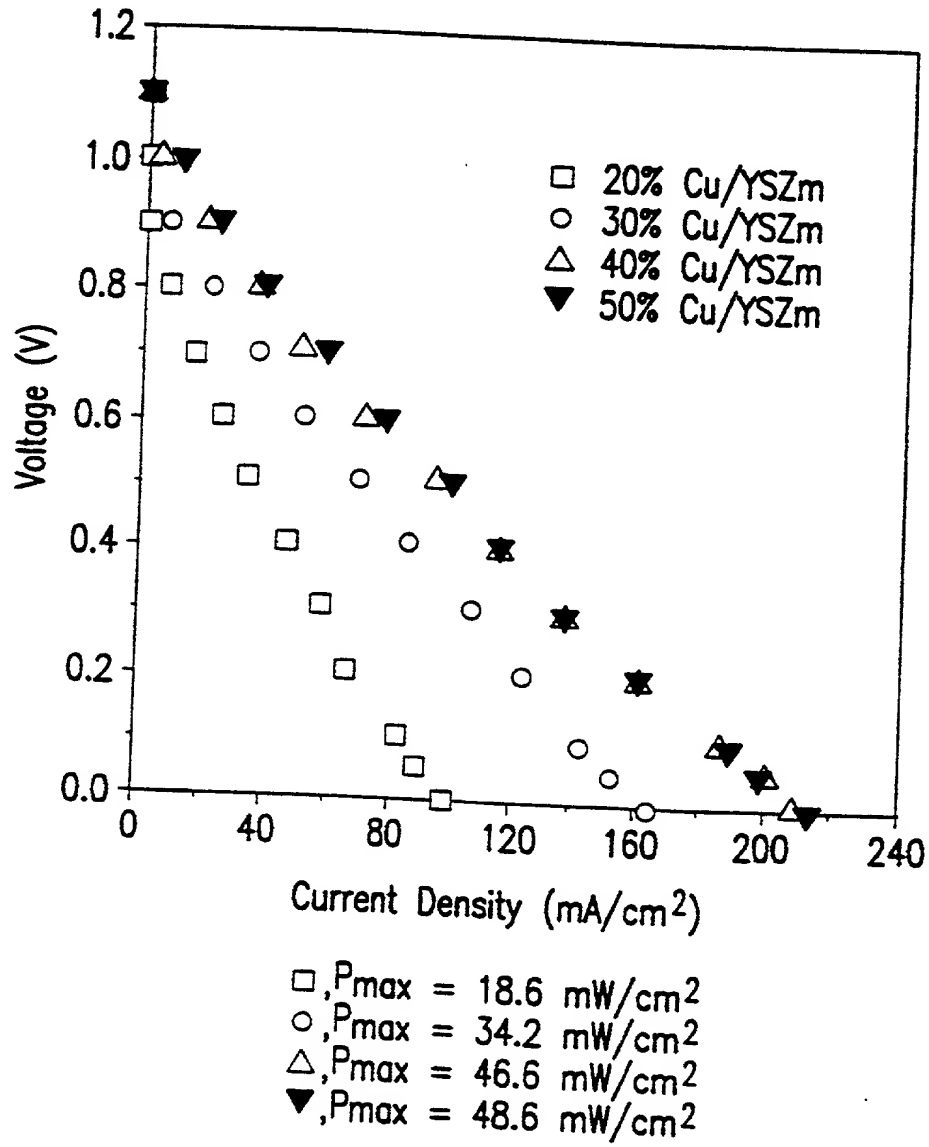


FIG.3

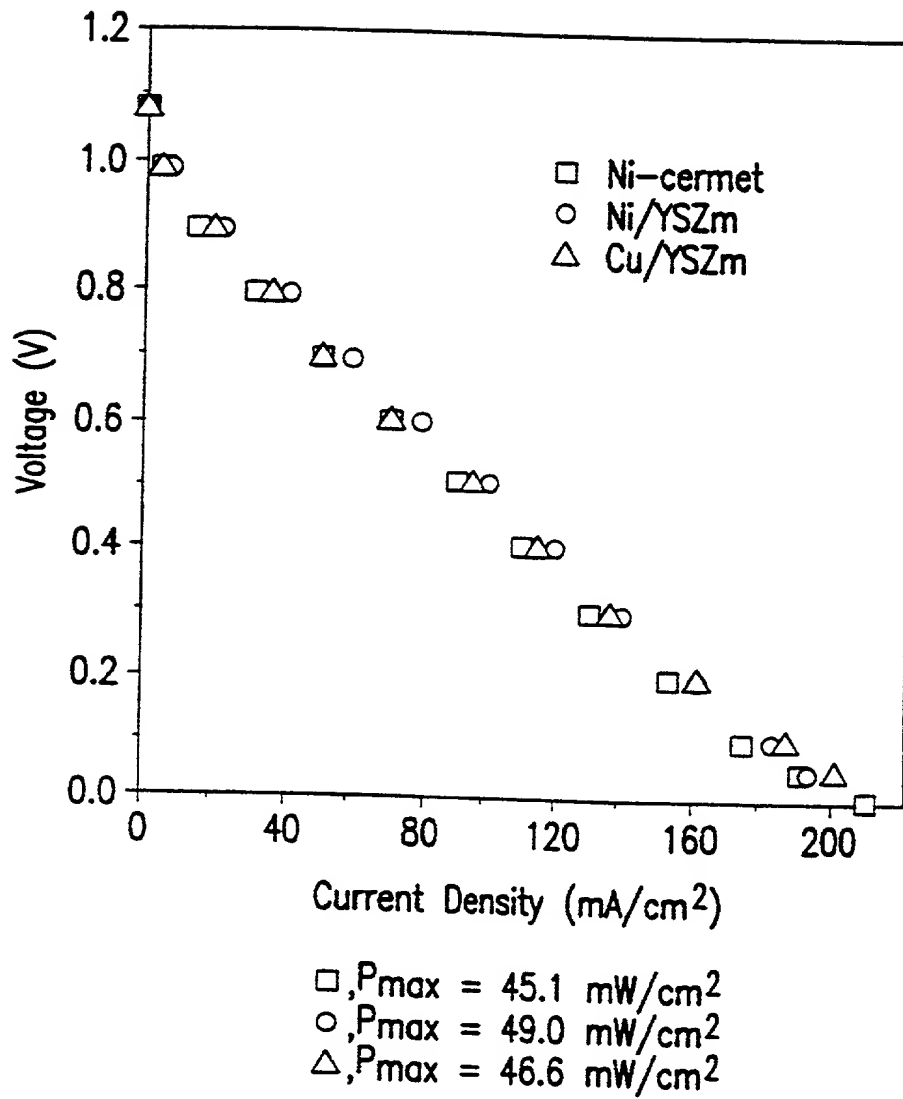


FIG.4

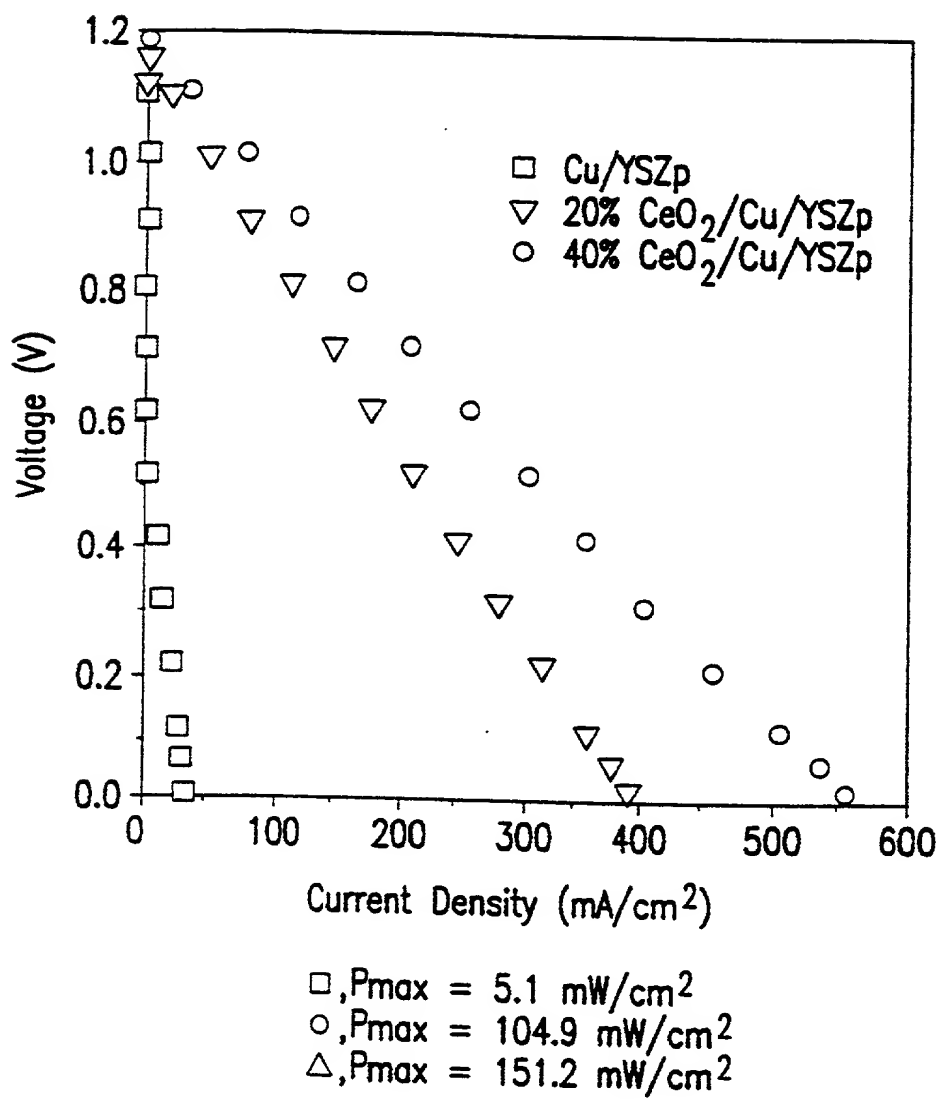


FIG.5

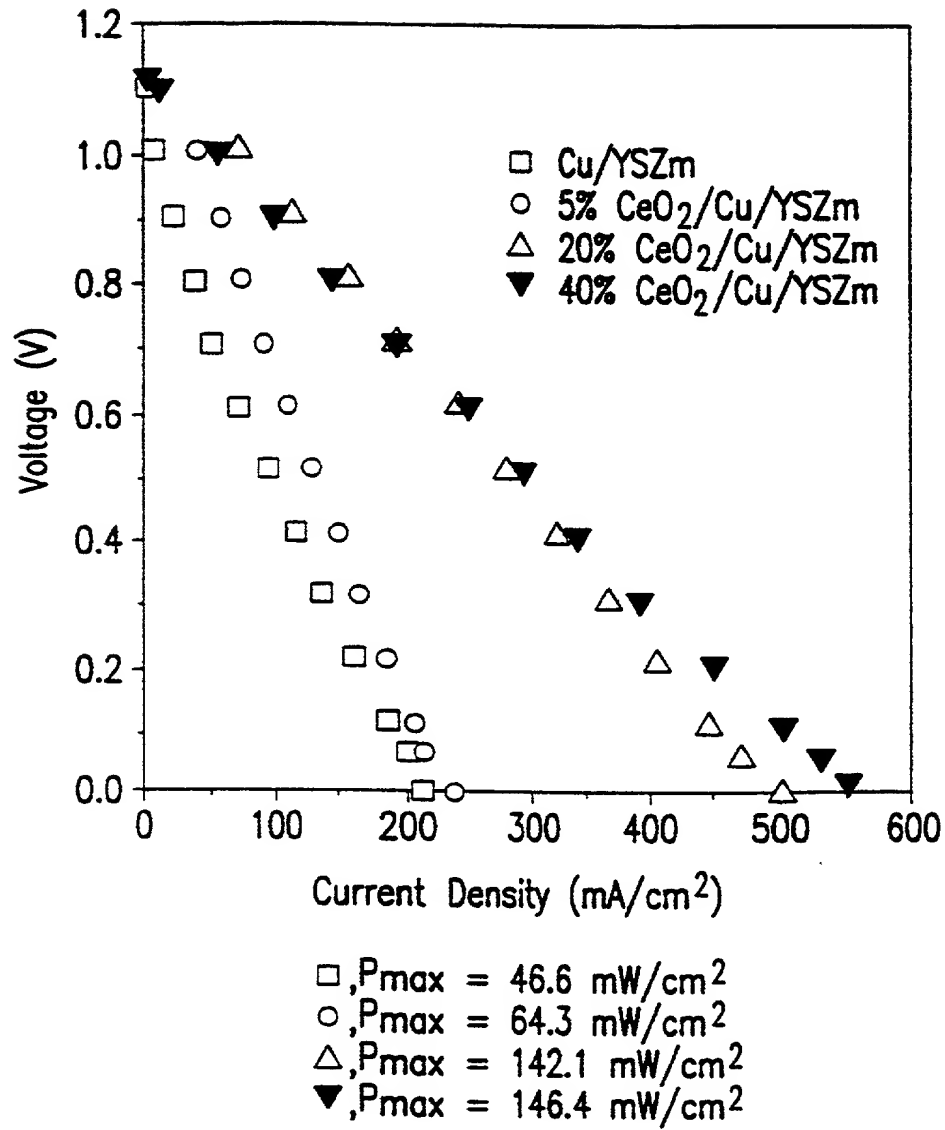


FIG.6

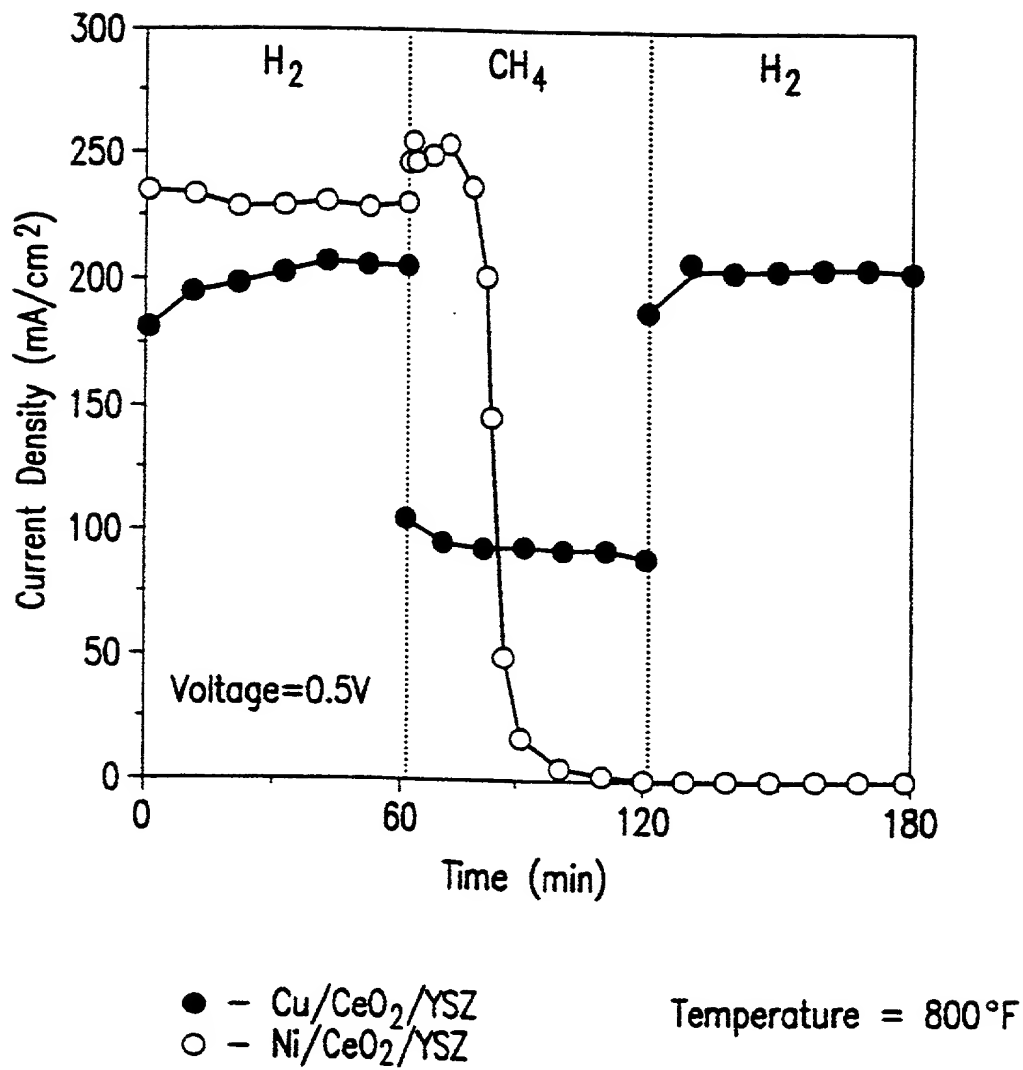


FIG.7

FIG.8

PATENT COOPERATION TREATY

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NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

FEJER, Mark, E.
Pauley Petersen Kinne & Fejer
Suite 365
2800 West Higgins Road
Hoffman Estates, IL 60195
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 05 December 2000 (05.12.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference GRI-98024PCT	
International application No. PCT/US00/05735	International filing date (day/month/year) 03 March 2000 (03.03.00)

1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

Name and Address CRACIUN, Radu 3426 Bailey Creek Cove South Collierville, TN 38109 United States of America	State of Nationality US	State of Residence US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☐ the address ☒ the nationality ☐ the residence

Name and Address CRACIUN, Radu 3426 Bailey Creek Cove South Collierville, TN 38109 United States of America	State of Nationality RO	State of Residence US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

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The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Maria Victoria CORTIELLO Telephone No.: (41-22) 338.83.38
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CHANGE OF CORRESPONDENCE ADDRESS <i>Application</i> Address to: Assistant Commissioner for Patents Washington, D.C. 20231	Application Number	09/914,638
	Filing Date	
	First Named Inventor	GORTE, R
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRI-01-013

Please change the Correspondence Address for the above-identified application to.

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OR

<input checked="" type="checkbox"/> Firm or Individual Name	Mark E. Fejer				
Address	Gas Technology Institute				
Address	1700 South Mount Prospect Road				
City	Des Plaines	State	Illinois	ZIP	60018
Country	United States of America				
Telephone	(847) 768-0832	Fax	(847) 768-0802		

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I am the :

☐ Applicant/Inventor.

☐ Assignee of record of the entire interest.
Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

☒ Attorney or Agent of record.

☐ Registered practitioner named in the application transmittal letter in an application without an executed oath or declaration. See 37 CFR 1.33(a)(1). Registration Number _____

Typed or Printed Name	Mark E. Fejer (Regis. No. 34,817)
Signature	<i>Mark E. Fejer</i>
Date	30 November 2001
NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below*.	
<input type="checkbox"/> *Total of _____ forms are submitted.	

Burden Hour Statement This form is estimated to take 3 minutes to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231 DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS SEND TO Assistant Commissioner for Patents, Washington, DC 20231

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Date of Deposit 30 November 2001

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COMBINED DECLARATION, POWER
OF ATTORNEY AND PETITION

SEND CORRESPONDENCE TO:

Mark E. Fejer
 Pauley Petersen Kinne & Fejer
 2800 West Higgins Road; Suite 365
 Hoffman Estates, Illinois 60195
 FAX (847) 490-1403

DIRECT TELEPHONE CALLS TO:

Mark E. Fejer
 (847) 490-1400

PETITION

Wherefore we Pray that Letters Patent be granted to us for the invention or discovery described and claimed in the specification and claims of U.S. Patent Application Serial No. 09/914,638, and we hereby subscribe our names to the specification and claims of U.S. Patent Application Serial No. 09/914,638, Declaration, Power of Attorney and this Petition.

DECLARATION

The undersigned further declare that all statements made herein of their knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

12/5/01
 Date

Raymond J. Gorte
 Raymond J. GORTE

12/5/01
 Date

John M. VoHS
 John M. VOHS

 Date

 Radu CRACIUN

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 12/21/01
 10:44:00

PATENT COOPERATION TREATY

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NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

FEJER, Mark, E.
Pauley Petersen Kinne & Fejer
Suite 365
2800 West Higgins Road
Hoffman Estates, IL 60195
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 24 September 2001 (24.09.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference GRI-98024PCT	
International application No. PCT/US00/05735	International filing date (day/month/year) 03 March 2000 (03.03.00)

1. The following indications appeared on record concerning:

☒ the applicant
 ☐ the inventor
 ☐ the agent
 ☐ the common representative

Name and Address GAS RESEARCH INSTITUTE 8600 West Bryn Mawr Avenue Chicago, IL 60631 United States of America	State of Nationality US	State of Residence US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person
 ☐ the name
 ☐ the address
 ☐ the nationality
 ☐ the residence

Name and Address THE TRUSTEES OF THE UNIVERSITY OF PENNSYLVANIA 3700 Market Street Suite 300 Philadelphia, PA 19104-3147 United States of America	State of Nationality US	State of Residence US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

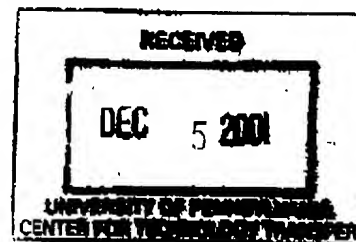
<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Ning XU Telephone No.: (41-22) 338.83.38
--	--

09914633 422704

COMBINED DECLARATION, POWER OF ATTORNEY AND PETITION

We, the inventors,



1. Name: Raymond J. GORTE
 Residence: Narberth, Pennsylvania
 Post Office Address: 512 Broad Acres Road
 Narberth, Pennsylvania 19072
 Citizenship: United States of America
2. Name: John M. VOHS
 Residence: Newtown Square, Pennsylvania
 Post Office Address: 45 Sawgrass Lane
 Newtown Square, Pennsylvania 19073
 Citizenship: United States of America
3. Name: Radu CRACIUN
 Residence: ~~Collierville, Tennessee~~ CARMEL - NY.
 Post Office Address: ~~3426 Bailey Creek Cove, South Collierville, Tennessee 38109~~ 87 MAJESTIC RIDGE
 CARMEL NY - 10512
 Citizenship: Romania (Radu Craciun)

declare that we have reviewed and understand the contents of the specification and claims of U.S. Patent Application Serial No. 09/914,638, and we verily believe that we are the original, first and joint inventors or discoverers of the invention or discovery in

METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

described and claimed in an application for Letters Patent of the United States having Serial No. 09/914,638; that this application in part discloses and claims subject matter disclosed in our earlier filed pending application(s) of which we hereby claim the benefit under 35 U.S.C., Section 120, Serial No. 09/261,324, filed 03 March 1999; that as to the subject matter of this application which is common to any said earlier application(s), we do not know and do not believe that the same was ever known or used in the United States before our invention or discovery thereof; that to the best of our knowledge and belief the invention of said common subject matter has not been in public use or on sale in the United States more than one year prior to the earliest of said application(s) or patented or described in any printed publication in any country before our invention thereof or more than one year prior to the earliest of said application(s), or patented or made the subject of an inventors' certificate in any foreign country prior to the date of the earliest of said application(s) on an application filed by ourselves or our legal representatives or assigns more than twelve months prior to the earliest of said application(s) in this country; and that no application for patent or inventors' certificate on the invention or discovery of said common subject matter

09/914,638 12/27/01

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has been filed by us or our legal representatives or assigns in any country foreign to the United States, except as follows:

PCT/US00/05735 03 March 2000

that as to the subject matter of this application which is not common to said earlier application(s), we do not know and do not believe that the same was ever known or used in the United States before our invention or discovery thereof; that to the best of our knowledge and belief the invention thereof has not been in public use or on sale in the United States more than one year prior to this application or patented or described in any printed publication in any country before our invention thereof or more than one year prior to this application, or patented or made the subject of an inventors' certificate in any foreign country prior to the date of this application on an application filed by ourselves or our legal representatives or assigns more than twelve months prior to this application in this country; that we acknowledge our duty to disclose information of which we are aware which is material to the examination of this application in accordance with 37 C.F.R. 1.56(a); that, insofar as the subject matter of each of the claims of this application is not disclosed in said earlier application(s) in the manner provided by 35 U.S.C. Section 112, first paragraph, we acknowledge our duty to disclose information that is material to examination of this application which occurred between the filing date of said earlier pending application(s) relied upon under 35 U.S.C. 120 and the filing date of this application, and that no application for patent or inventors' certificate on this invention or discovery has been filed by us or our legal representatives or assigns in any country foreign to the United States, except as follows:

None

POWER OF ATTORNEY

We hereby appoint the following attorneys to prosecute this application and transact all business in the United States Patent and Trademark Office connected therewith:

Thomas W. Speckman	Registration No. 22,617
Douglas H. Pauley	Registration No. 33,295
Maxwell J. Petersen	Registration No. 32,772
Charles C. Kinne	Registration No. 31,631
Mark E. Fejer	Registration No. 34,817
Nick C. Kottis	Registration No. 31,974
Kevin D. Erickson	Registration No. 38,736
Roland W. Norris	Registration No. 32,799
Melanie I. Rauch	Registration No. 40,924
Eric T. Krischke	Registration No. 42,769
Margaret M. Crosby	Registration No. 40,969

COMBINED DECLARATION, POWER
OF ATTORNEY AND PETITION

SEND CORRESPONDENCE TO:

Mark E. Fejer
Pauley Petersen Kinne & Fejer
2800 West Higgins Road; Suite 365
Hoffman Estates, Illinois 60195
FAX (847) 490-1403

DIRECT TELEPHONE CALLS TO:

Mark E. Fejer
(847) 490-1400

PETITION

Wherefore we Pray that Letters Patent be granted to us for the invention or discovery described and claimed in the specification and claims of U.S. Patent Application Serial No. 09/914,638, and we hereby subscribe our names to the specification and claims of U.S. Patent Application Serial No. 09/914,638, Declaration, Power of Attorney and this Petition.

DECLARATION

The undersigned further declare that all statements made herein of their knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date

Raymond J. GORTE

Date

John M. VOHS

Dec. 04. 2001

Date

Radu Craciun

Radu CRACIUN

COMBINED DECLARATION, POWER OF ATTORNEY AND PETITION

We, the inventors,

1. Name: Raymond J. GORTE
 Residence: Narberth, Pennsylvania
 Post Office Address: 512 Broad Acres Road
Narberth, Pennsylvania 19072 PA
 Citizenship: United States of America
2. Name: John M. VOHS
 Residence: Newtown Square, Pennsylvania
 Post Office Address: 45 Sawgrass Lane
Newtown Square, Pennsylvania 19073 PA
 Citizenship: United States of America
3. Name: Radu CRACIUN
 Residence: Collierville, Tennessee TN
 Post Office Address: 3426 Bailey Creek Cove, South
Collierville, Tennessee 38109
 Citizenship: Romania

declare that we have reviewed and understand the contents of the specification and claims of U.S. Patent Application Serial No. 09/914,638, and we verily believe that we are the original, first and joint inventors or discoverers of the invention or discovery in

METHOD FOR SOLID OXIDE FUEL CELL ANODE PREPARATION

described and claimed in an application for Letters Patent of the United States having Serial No. 09/914,638; that this application in part discloses and claims subject matter disclosed in our earlier filed pending application(s) of which we hereby claim the benefit under 35 U.S.C., Section 120, Serial No. 09/261,324, filed 03 March 1999; that as to the subject matter of this application which is common to any said earlier application(s), we do not know and do not believe that the same was ever known or used in the United States before our invention or discovery thereof; that to the best of our knowledge and belief the invention of said common subject matter has not been in public use or on sale in the United States more than one year prior to the earliest of said application(s) or patented or described in any printed publication in any country before our invention thereof or more than one year prior to the earliest of said application(s), or patented or made the subject of an inventors' certificate in any foreign country prior to the date of the earliest of said application(s) on an application filed by ourselves or our legal representatives or assigns more than twelve months prior to the earliest of said application(s) in this country; and that no application for patent or inventors' certificate on the invention or discovery of said common subject matter

00014638-123701

COMBINED DECLARATION, POWER
OF ATTORNEY AND PETITION

has been filed by us or our legal representatives or assigns in any country foreign to the United States, except as follows:

PCT/US00/05735 03 March 2000

that as to the subject matter of this application which is not common to said earlier application(s), we do not know and do not believe that the same was ever known or used in the United States before our invention or discovery thereof; that to the best of our knowledge and belief the invention thereof has not been in public use or on sale in the United States more than one year prior to this application or patented or described in any printed publication in any country before our invention thereof or more than one year prior to this application, or patented or made the subject of an inventors' certificate in any foreign country prior to the date of this application on an application filed by ourselves or our legal representatives or assigns more than twelve months prior to this application in this country; that we acknowledge our duty to disclose information of which we are aware which is material to the examination of this application in accordance with 37 C.F.R. 1.56(a); that, insofar as the subject matter of each of the claims of this application is not disclosed in said earlier application(s) in the manner provided by 35 U.S.C. Section 112, first paragraph, we acknowledge our duty to disclose information that is material to examination of this application which occurred between the filing date of said earlier pending application(s) relied upon under 35 U.S.C. 120 and the filing date of this application, and that no application for patent or inventors' certificate on this invention or discovery has been filed by us or our legal representatives or assigns in any country foreign to the United States, except as follows:

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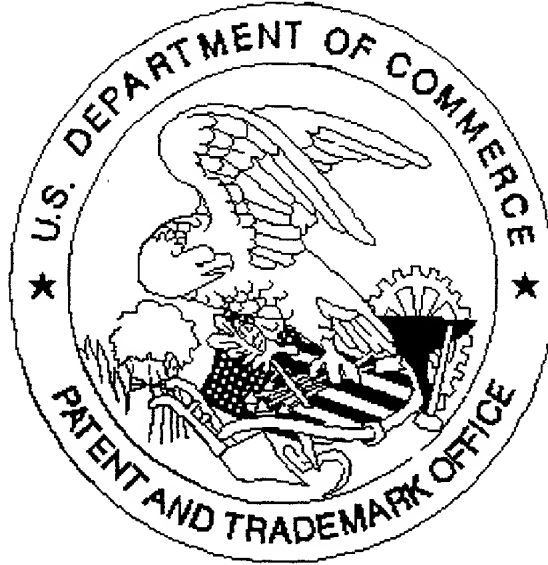
POWER OF ATTORNEY

We hereby appoint the following attorneys to prosecute this application and transact all business in the United States Patent and Trademark Office connected therewith:

Thomas W. Speckman	Registration No. 22,617
Douglas H. Pauley	Registration No. 33,295
Maxwell J. Petersen	Registration No. 32,772
Charles C. Kinne	Registration No. 31,631
Mark E. Fejer	Registration No. 34,817
Nick C. Kottis	Registration No. 31,974
Kevin D. Erickson	Registration No. 38,736
Roland W. Norris	Registration No. 32,799
Melanie I. Rauch	Registration No. 40,924
Eric T. Krischke	Registration No. 42,769
Margaret M. Crosby	Registration No. 40,969

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